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Research Article

Microbial-induced remediation of Zn^{2+} pollution based on the capture and utilization of carbon dioxide

Qiwei Zhan, Chunxiang Qian *

School of Materials Science and Engineering, Southeast University, Jiulonghu Campus, Nanjing 211189, People's Republic of China
 Research Institute of Green Construction Materials, Southeast University, Jiulonghu Campus Nanjing 211189, People's Republic of China

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ABSTRACT

Background: Microbial-induced remediation of Zn^{2+} pollution based on the capture and utilization of carbon dioxide was investigated. In this study, carbon dioxide was absorbed and transformed into carbonate ions under the enzymatic action of *Paenibacillus mucilaginosus*, which was being utilized to mineralize Zn^{2+} .

Results: The compositional and morphological properties of the precipitations were studied using Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The thermal properties of the precipitates were investigated by thermogravimetric-differential scanning calorimetry (TG-DSC). The FTIR results confirmed that the functional groups of the precipitates were CO_3^{2-} and OH^- . The XRD and EDS patterns showed that basic zinc carbonate could be obtained successfully by Microbial-induced remediation. The SEM micrographs demonstrated that the precipitates were in the nanometer range with sizes of 100–200 nm and were sphere-like in shape.

Conclusions: The TG-DSC results showed that weight loss of the precipitates occurred around 253°C. The FTIR and TG-DSC results were in accord with the XRD and EDS results and proved again that the precipitates were basic zinc carbonate. This work thus demonstrates a new method for processing Zn^{2+} pollution based on the utilization of carbon dioxide.

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1. Introduction

Technology advances and environmental requirements become more stringent, for this reason, the control of carbon dioxide emissions has become a necessary task for energy suppliers and industries [1,2,3]. Currently, carbon dioxide capturing systems and carbon dioxide separation technologies are the focus of much research. Many experts and scholars have begun to study carbon dioxide utilization by microorganisms in detail, as it shows promise for future efforts aimed at carbon dioxide emission reductions [4,5,6,7]. With rapid urban development and industrialization, heavy metal pollution has become more serious than ever before. In general, three measures can be taken to control and remedy aromatic organic compounds and heavy metal pollution-physical methods, chemical methods, and biological methods [8,9,10,11,12]. Because of the associated high energy consumption, large investment costs, complex operational procedures, and likely secondary pollution to the environment, physical and chemical methods are relatively

difficult to apply when remediating soil pollution over large areas [13, 14]. Thus, biological methods, which typically produce stable and reliable results with no secondary pollution, have become the most promising method for the large-scale remediation of heavy metals [15,16,17,18,19,20,21].

The free state of heavy metals can be migrated which is harmful. This paper mainly aimed at the remediation of free state Zn^{2+} pollution. The Zn precipitate, basic zinc carbonate is a solid precipitate, and its character is stable in the neutral and alkaline environment. Therefore, the formation of basic zinc carbonate could effectively prevent heavy metal ions from migration. Only in an acid environment, basic zinc carbonate was dissolved, and zinc ions could be free migration. The results of microbial-induced remediation of Zn^{2+} pollution provide references for future applications in a real soil Zn^{2+} pollution and other heavy metal pollution. In this research, *Paenibacillus mucilaginosus* was selected as the target organism, and this choice was based on the results of a previous study [22]. In that study, carbon dioxide was absorbed and transformed into carbonate ions under the carbonic anhydrase action of *P. mucilaginosus*, which was being utilized to mineralize Zn^{2+} . Here, investigations were conducted on the precipitations that formed during the reactions mediated by microbial-induced remediation; these precipitates largely consisted of zinc carbonate. Specifically, the composition,

* Corresponding author at: School of Materials Science and Engineering, Southeast University, Jiulonghu Campus Nanjing 211189, People's Republic of China.

E-mail address: cxqian@seu.edu.cn (C. Qian).

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morphology, and thermal decomposition properties of the precipitates were characterized by Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric-differential scanning calorimetry (TG-DSC).

2. Materials and methods

All the materials, which were obtained from commercial sources, were used without further purification. The *P. mucilaginosus* culture was purchased from the China Center of Industrial Culture Collection (CCIC), and the culture had an OD600 value of 1.2 and an enzyme activity value of $0.9 \text{ mmol} \cdot \text{L}^{-1}$. Cultivation of *P. mucilaginosus* was conducted in sucrose culture media (15 g of sucrose and 5 g of sodium hydrogen phosphate were dissolved in deionized water in a final volume of 1 L, and the pH value was adjusted with $600 \text{ mmol} \cdot \text{L}^{-1}$ NaOH to about 8.0) at 35°C for 24 h. Then, the harvested microorganisms were kept in a refrigerator at 4°C as a stock culture prior to their use.

A total of 200 mL of $150 \text{ mmol} \cdot \text{L}^{-1}$ ZnSO_4 was prepared for the experiments, and 50 mL *P. mucilaginosus* culture was added to the above solution. Next, 99% of carbon dioxide was piped continuously into the mixed solution from a carbon dioxide storage device, and the reaction was allowed to proceed for 72 h. The precipitates that formed were filtered out of the solution and washed three times with deionized water and ethanol; then, the precipitates were dried at 60°C in an oven. Afterward, the precipitates were collected and characterized.

The FTIR spectrum of the precipitations was recorded using a Nicolet 5700 spectrometer by KBr pellet technique with the resolution of 4 cm^{-1} and scanning the product for 20 times in the range of $4000\text{--}400 \text{ cm}^{-1}$. The precipitate was examined by XRD with Bruker D8-Discover diffractometer using graphite monochromatized high-intensity $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The scanning angle range was from 10° to 90° 2θ with the step at $0.2^\circ \cdot \text{step}^{-1}$. SEM (FEI Company, Netherlands) with a GENESIS 60S EDS spectroscopy system with magnification from 5000 to 200,000 was used to observe the morphology and to measure the elemental compositions of the precipitations. The accelerating voltage and spot size of the secondary electron detector were 20 kV and 4.0, respectively. TG-DSC analysis was carried out on the STA449 F3 thermogravimetric analyzer (Netzsch, Germany). These analyzes were carried out simultaneously in a nitrogen atmosphere at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ between room temperature and 1000°C .

3. Results and discussion

3.1. FTIR analysis

The FTIR spectrum was used effectively to identify the functional groups of the precipitates, and the FTIR spectrum results are shown in Fig. 1. The vibrational absorptions that appeared at 739 and 1342 cm^{-1} can be attributed to CO_3^{2-} . The data show strong vibrational absorptions for OH^- stretching at 1524 cm^{-1} . A wide band of crystal H_2O at around 3352 cm^{-1} was observed in the FTIR analysis data for the samples. Strong transmission bands for SO_4^{2-} were reflected in the data at 496 and 1089 cm^{-1} , which may have come from the reaction of raw materials in the ZnSO_4 and, therefore, should not be attributed to the functional groups of the precipitations. The above results confirm that the primary functional groups of the precipitations were CO_3^{2-} and OH^- .

3.2. EDS and XRD analysis

An elemental analysis of the precipitate composition was performed by using EDS, and the results are shown in Fig. 2. These data confirm the

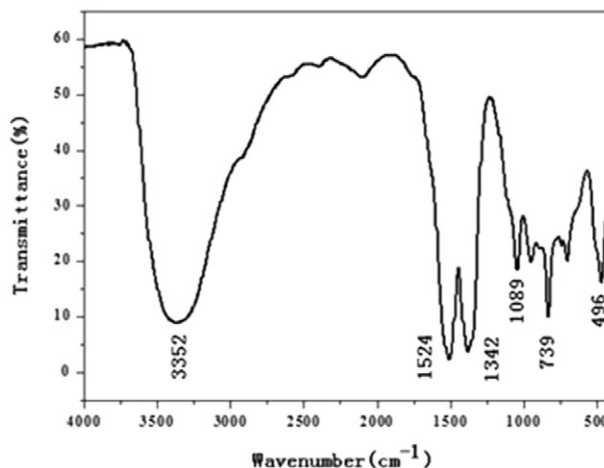


Fig. 1. FTIR spectra of the precipitates obtained by microbial-induced remediation.

presence of elements O, C, and Zn. The XRD patterns of precipitates obtained from samples subjected to microbial-induced remediation are shown in Fig. 3. It should be noted that the peaks in the XRD pattern were in good agreement with the results for the standard (JCPDS card number 19-1458), and the precipitates were ultimately characterized as basic zinc carbonate. Compared with the diffraction peak intensity reported in the literature [23], the one detected here was lower. It is well known that microbial activity can have an effect on crystal growth and lead to poor crystallinity [24].

3.3. SEM analysis

The SEM micrographs of the precipitates are shown in Fig. 4. As Fig. 4 shows, the overall evaluation of the morphology revealed a suitable and uniform distribution of nanoparticles within large agglomerates of basic zinc carbonate. The shapes of the precipitates were sphere-like and in the nanometer range with particle sizes of 100–200 nm.

3.4. TG-DSC analysis

The thermal stability of the precipitates was determined by thermogravimetric analysis in a nitrogen atmosphere, and the results are shown in Fig. 5. Two obvious weight loss behaviors corresponded to respective thermal changes in the DSC curves. The first DSC peak occurred at around 92°C , which may have been from the crystal water, and the corresponding weight loss was 3.21%. The second peak that took place at around 253°C was a result of the crystalline properties of basic zinc carbonate, which decomposes at temperatures between 236°C to 262°C ; the corresponding weight loss was about 20.66%, and there was no significant weight loss over 300°C . These data indicate that the thermal decomposition temperature of basic zinc carbonate is about 253°C , which is in accord with the reports in the literature [23].

3.5. Mechanism of remediation

Microbial-induced remediation of Zn^{2+} pollution is based on the capture and utilization of carbon dioxide, and it involves relatively complex physical and chemical processes. In this study, *P. mucilaginosus* was employed. First, carbon dioxide was absorbed and transformed into bicarbonate ions under the enzymatic action of *P. mucilaginosus*. Second, bicarbonate ions were transformed into carbonate ions under the condition of the alkaline environment. Meanwhile, Zn^{2+} pollution in the solution were attracted to the bacteria cell walls due to their negative charges upon introduction of the substrate to the bacteria. Finally, Zn^{2+} pollution were mineralized

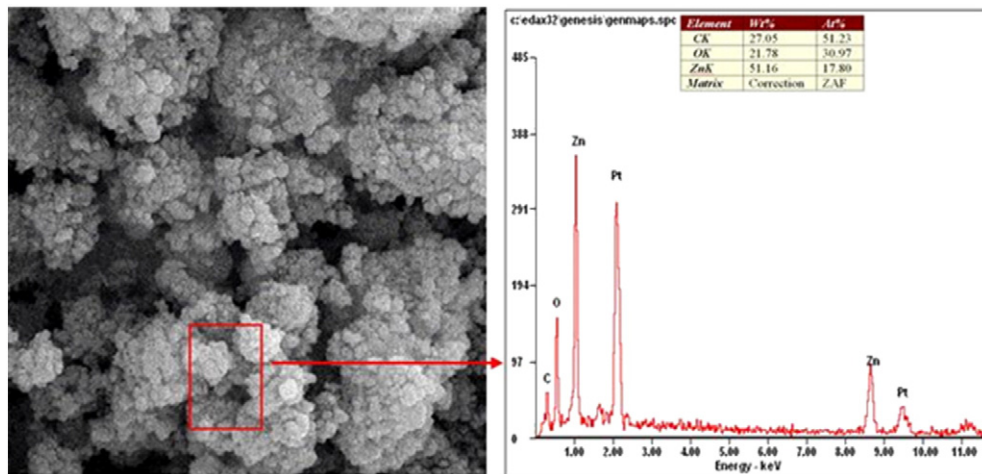


Fig. 2. EDS analysis of the precipitates obtained by microbial-induced remediation.

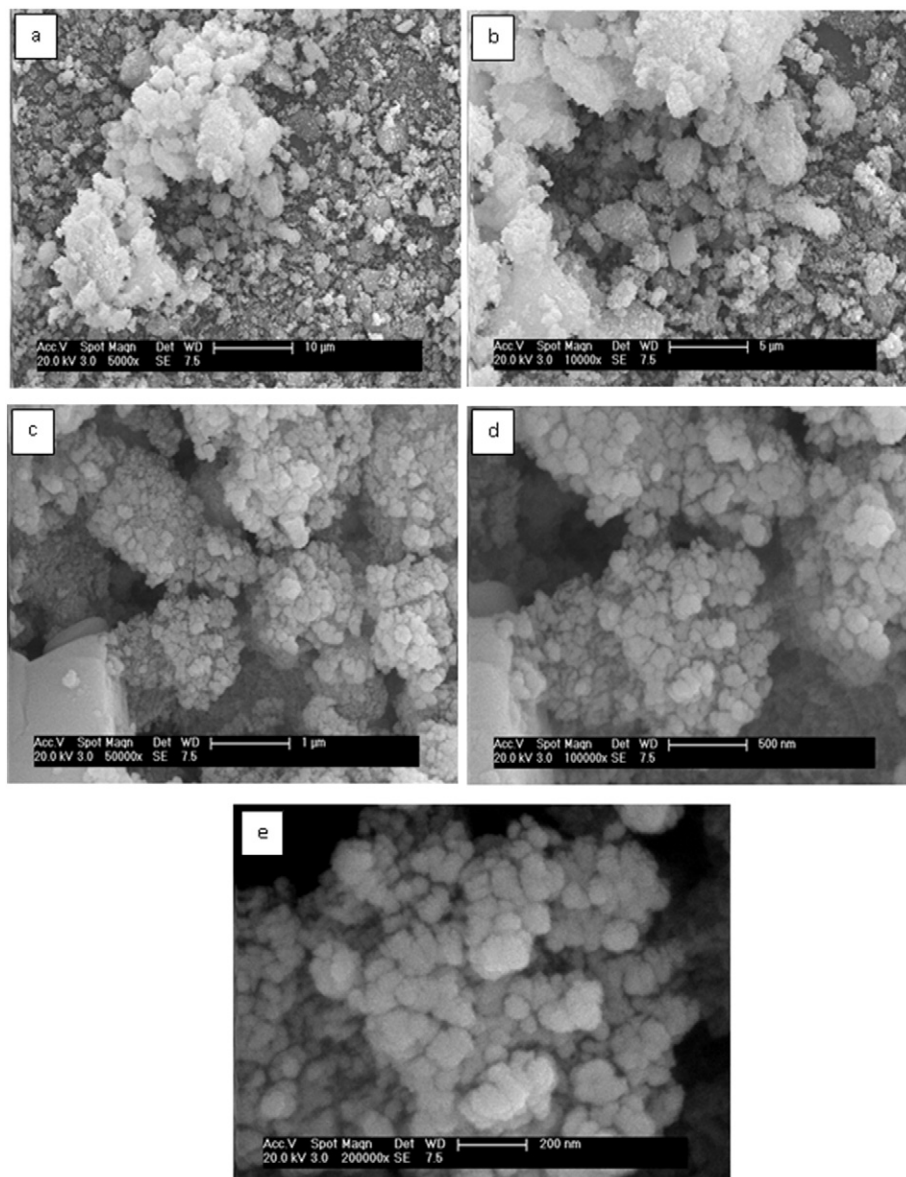


Fig. 3. The XRD patterns of the precipitates obtained by microbial-induced remediation.

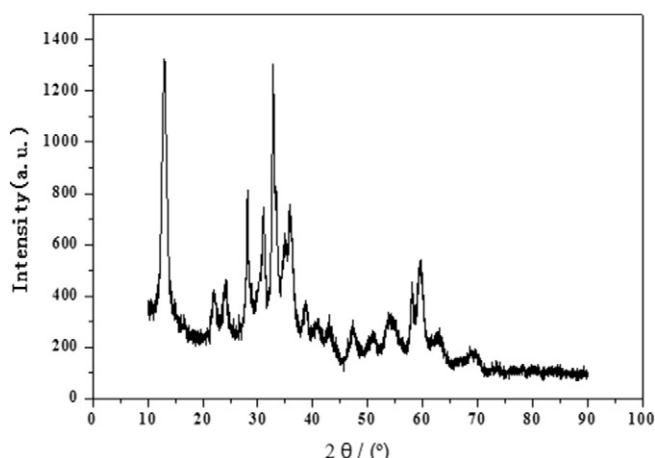


Fig. 4. SEM images of the precipitations obtained by microbial-induced remediation (a: 5000×, b: 10000×, c: 50000×, d: 100000×, e: 200000×).

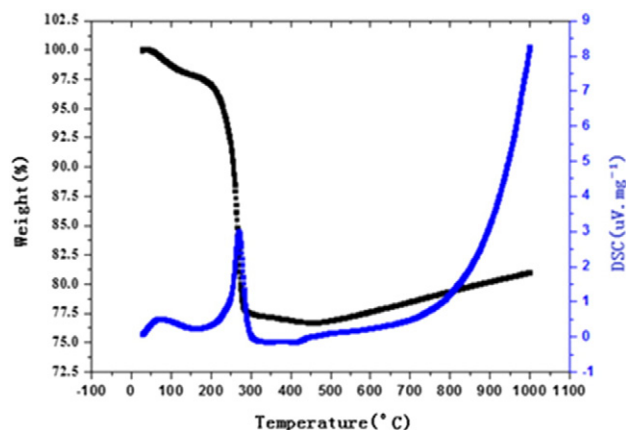
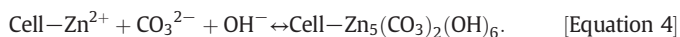


Fig. 5. Thermal analysis curves of the precipitations obtained by microbial-induced remediation.

and precipitated to carbonate particles at the cell surfaces, which served as nucleation sites. The mechanism of microbial-induced remediation of Zn^{2+} pollution based on the capture and utilization of carbon dioxide can be explained by the following equations:



4. Conclusions

This research showed that Zn^{2+} pollution could be remediated by microbial-induced remediation based on the capture and utilization of carbon dioxide. In this process, carbon dioxide was absorbed and transformed into carbonate ions under the enzymatic action of *P. mucilaginosus*, which could mineralize Zn^{2+} into carbonate precipitations. The precipitates were ultimately characterized as basic zinc carbonate. The FTIR spectra, EDS data, and XRD diffraction graphs confirmed the structure of the precipitates,

and SEM morphology analysis revealed that they were in the nanometer range with sizes of 100–200 nm and were sphere-like in shape. The thermal decomposition temperature of the precipitates was about 253°C, which is coherent with basic zinc carbonate. Thus, this new method may provide a new way to remedy Zn^{2+} pollution and utilize carbon dioxide simultaneously.

Conflict of interest

The authors declare that there are no conflict of interest.

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